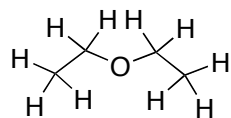
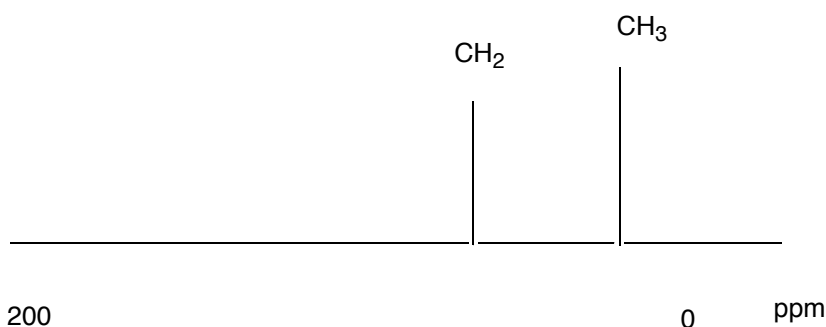


Nuclear Magnetic Resonance (NMR) (Continuation of Jan 12 lecture)

NMR is not a chiral technique. It cannot distinguish between enantiomers but can distinguish between diastereomers.

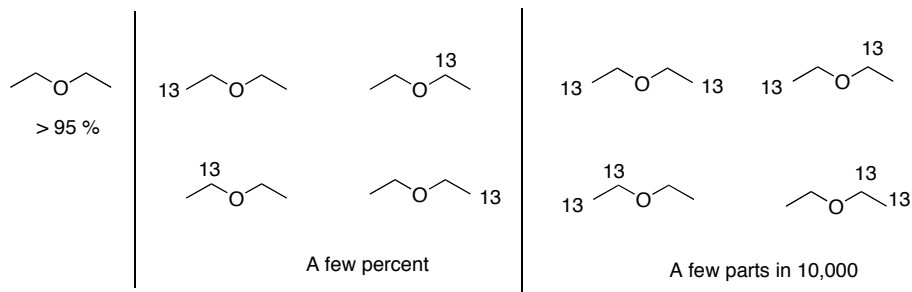
 ^{13}C NMR spectrum of

diethyl ether



^{13}C NMR spectra are run decoupled (irradiate at the proton frequency to remove the ^{13}C to ^1H spin-spin coupling) so that the ^{13}C signals appear as singlets. This makes the spectra easier to interpret.

The natural abundance of ^{13}C is 1.1%, so the chance of two ^{13}C 's being beside each other and coupling is small (0.01×0.01 or one part in ten thousand). A normal sample of a compound is a mixture of molecules that contain mostly ^{12}C at individual carbons and some ^{13}C (1.1% chance). Remember that ^{12}C is invisible in NMR. Thus a sample of ethyl ether will have a vast majority of all molecules having ^{12}C at each carbon. A small proportion of the molecules will have ^{13}C at one of the methyls (CH_3) and an equally small proportion will have ^{13}C at one of the methylenes (CH_2). Finally a much smaller proportion will have two ^{13}C atoms, or even three or four ^{13}C atoms in a given molecule.)



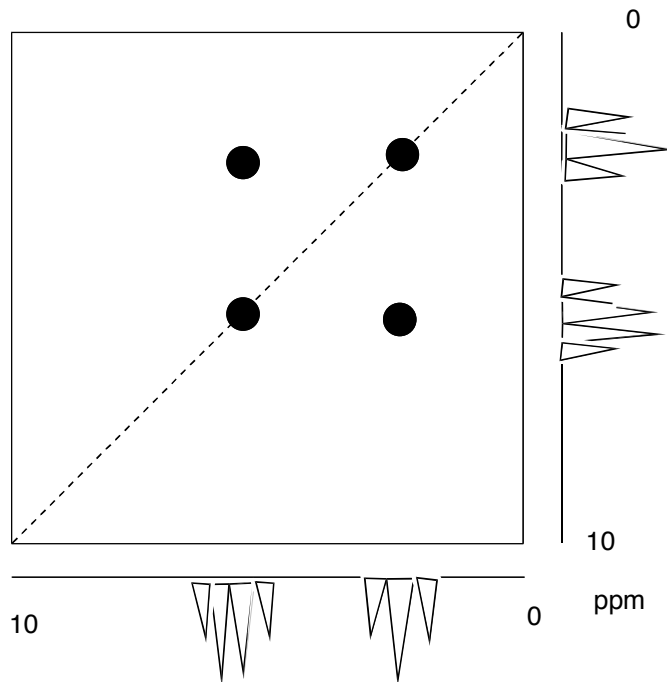
In ^1H NMR spectra, the relative area of the peaks indicates how many H's are present. In ^{13}C NMR spectra, the intensity or area of the peak cannot be used to calculate the relative number of carbons because of relaxation effects and transfer of energy from decoupled hydrogens.

2-D NMR

Correlation Spectroscopy (COSY)

Shown below is a COSY spectra of diethyl ether.

The off diagonal cross peaks show that the triplet and the quartet correlate to each other and the hydrogens that are responsible for those signals are on adjacent atoms (i.e. coupled) in the molecule. For a simple molecule like diethyl ether, this is trivial and can be seen from the one dimensional spectrum. However, in complex molecules with many triplets and quartets etc., the connectivity of coupled hydrogens can be determined.

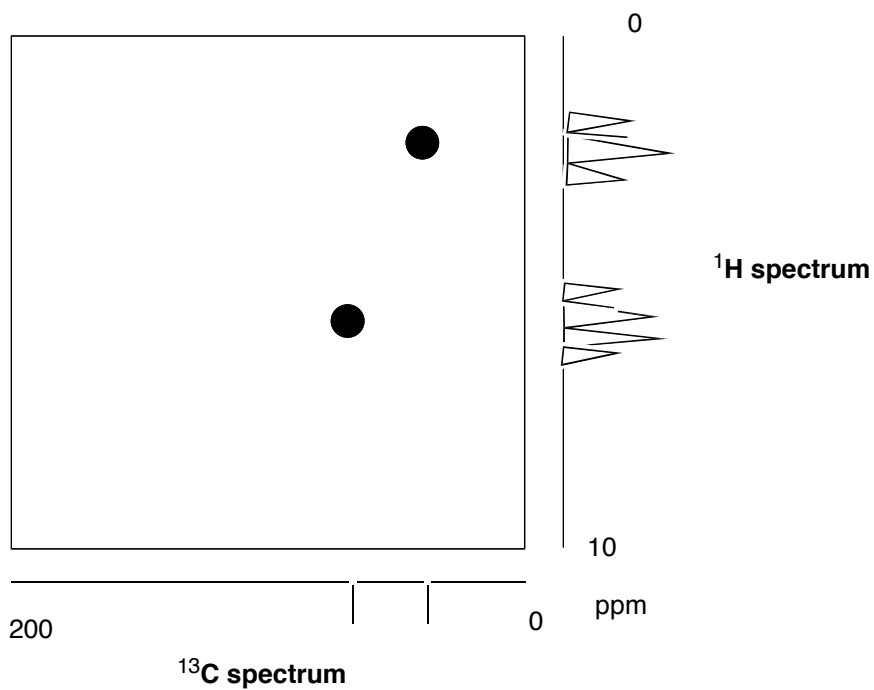


Heteronuclear Correlation Spectroscopy (HETCOR)

Shown below is the HETCOR spectra of diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$).

HETCOR shows which hydrogens are bonded to which carbons.

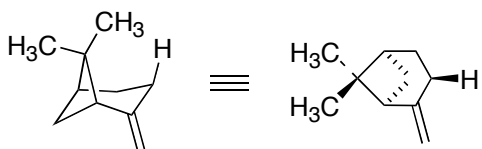
This technique correlates the ^1H NMR spectrum with the ^{13}C NMR spectrum. It allows connectivity patterns to be established in conjunction with COSY. In other words, COSY tells which hydrogens are adjacent to each other and HETCOR allows the connection to their respective carbons.



Nuclear Overhauser Effect (NOE)

An NOE effect is an energy transfer between two nuclei (e.g. protons) through space.

The effect drops off proportionally to $1/R^6$ where R = internuclear distance



beta-pinene: two drawings of the same molecule

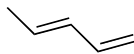
For better understanding of this structure, please see additional graphics page on our web site (www.chem.ualberta.ca/~vederas then click on basic organic chemistry) or use models available from first floor chemistry storeroom

This technique allows you to distinguish between the two methyl groups in beta-pinene (major constituent of turpentine). If the single diastereotopic H shown on the methylene is irradiated, it will transfer energy via the NOE effect to the closest methyl group and produce an enhanced signal. This will be shown by that one methyl group peak in the NMR spectrum becoming more intense. Irradiation of that same methyl will analogously enhance the methylene hydrogen shown. The more distant methyl will not show this NOE effect. This technique is useful for determining the 3-D orientation (structure) of molecules, including proteins. Three dimensional structures of proteins with 50,000 molecular weight and thousands of atoms have been determined by advanced versions of the NOE method.

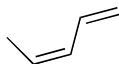
Conjugated systems (review and continuation of January 16 lecture by Dr. Tykwinski)

Review of nomenclature and examples

The two molecules below are stereoisomers.

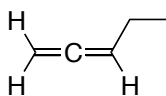


E-1,3-pentadiene

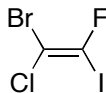


Z-1,3-pentadiene

The 1,2-pentadiene shown below is not conjugated. It has cumulated double bonds. This molecule is an allene and is a structural isomer with respect to the above 1,3-pentadienes.



Another example for nomenclature below: Is this an E or Z alkene (olefin)?



First of all, look at the highest priority (that is the highest atomic number of the atom directly attached) on either side of the double bond.

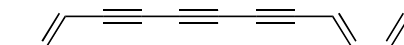
I is highest priority relative to F.

Br is highest priority relative to Cl

Therefore it is an E double bond as the high priority groups are on opposite sides of the double bond

It's name is (E)-1-bromo-1-chloro-2-fluoro-2-iodoethylene.

Another example for nomenclature below



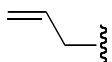
The above compound is part of a plant defense mechanism (anti-nematode) from canola to kill predatory worms.

All double bonds and triple bonds in the above compound are conjugated. Conjugated means the double bond (or triple bond) is separated by exactly one single bond from the next double or triple bond.

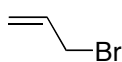
It is a derivative of a tridecane (13 carbons). Know the names of the first 20 alkanes (on handout in first class). Begin numbering at the end of the longest chain with maximum number of multiple bonds so as to give the first multiply bonded carbon the lowest number. The above compound would be named trideca-1,3E,11E-trien-5,7,9-triyne. There is no stereochemistry in the triple bond. Stereochemistry is only potentially possible in the double bonds.

Nomenclature of Allyl and Vinyl Group (the squiggly line represents attachment to any group)

Allyl Group



Example



allyl bromide

Vinyl Group

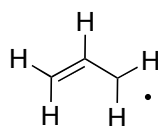
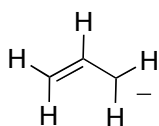
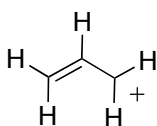


Example



vinyl chloride

Review of allyl intermediates:



allyl cation

allyl anion

allyl radical

has 6 e⁻ at positive carbon

has 8 e⁻ at negative carbon

has 7 e⁻ radical carbon

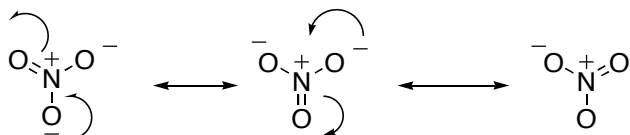
All are conjugated intermediates.

All are stabilized through resonance structures.

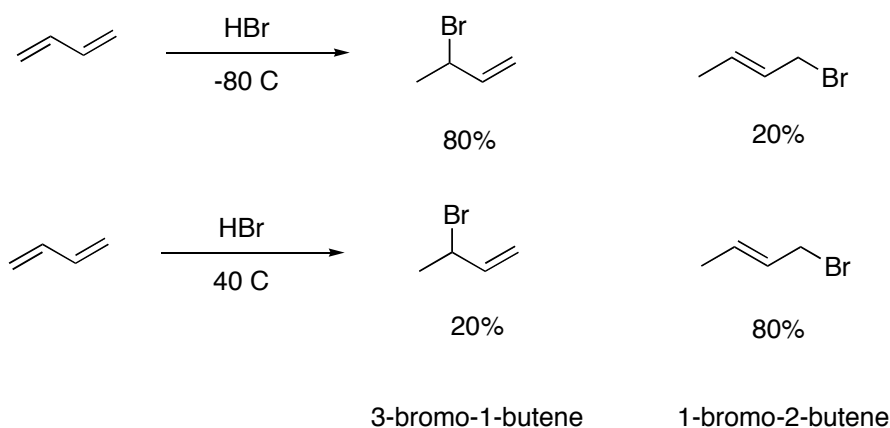
Resonance Forms

Resonance forms (resonance structures) are different picture of the same molecule obtained by moving electrons without changing the position of the atoms.

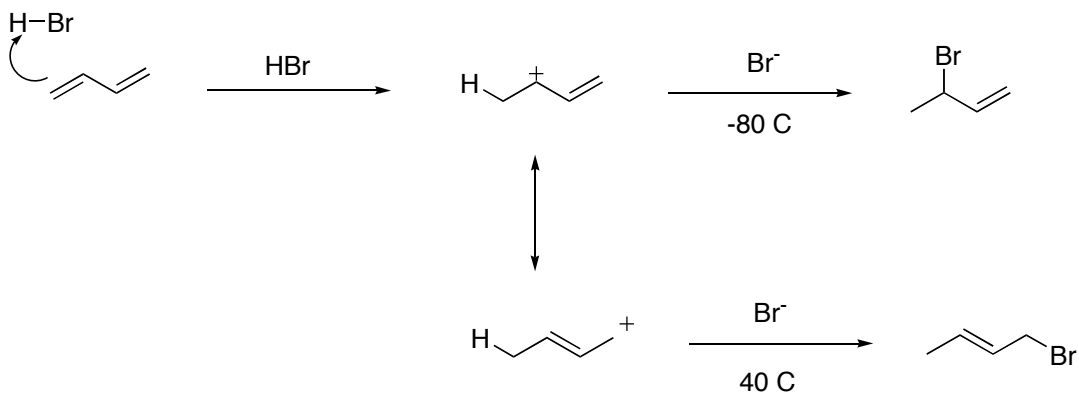
Shown below are the resonance forms of sodium nitrate (NaNO_3). The anion on oxygen is a conjugated anion. Resonance forms are connected by a double headed arrow.



Consider the reaction question posed by Dr. Tykwinski in the last class



WHY? To understand, look at mechanism of the reaction – see Solomons pages 605-606



Activation energy is the key: at low temperature the reaction proceeds by a low activation energy path, is NOT reversible, and an 80 to 20 distribution is seen by kinetic control. At

higher temperature the reaction is reversible (second pathway to be discussed) and displays thermodynamic control leading to the most stable distribution of products.